W. M. BAYLISS

SURFACE PHENOMENA IN LIVING STRUCTURES

REPRINT FROM "SCIENTIA,,
VOL. XIX, 10.th YEAR (1916), N. L-6
(June 1916)

BOLOGNA
NICOLA ZANICHELLI

LONDON
WILLIAMS AND NORGATE

PARIS
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22500883194

Si pubblica ogni mese.
Paraissant tous les mois.

1-VI-1916

Published monthly.
Erscheint alle Monate.

Anno - Année - Jahr - Year X.

Vol. - Band XIX, N. I-6

Serie - Série - Serie - Series II.

"SCIENTIA,,

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INDEX

S. Pincherle – *Il calcolo delle probabilità e l'intuizione* – *(Le calcul des probabilités et l'intuition).*

G. Bigourdan – *L'origine et les progrès de l'astronomie, en relation avec la mesure du temps et avec le problème des longitudes.*

W. M. Bayliss – *Surface phenomena in living structures* – *(Phénomènes de surface dans les structures vivantes).*

E. Ciccotti – *Dopo la guerra* – *(Après la guerre).*

J. G. K. Wicksell – *La guerre, la paix et l'accroissement de la population.*

Recensioni - Comptes rendus - Referate - Book Reviews.

V. Volterra, J. Hadamard, P. Langevin et P. Boutroux, *Henri Poincaré, l'œuvre scientifique, l'œuvre philosophique* **(M. Davidson).** — E. H. Starling, *Principles of Human Physiology* - E. W. Mac Bride, *Text-Book of Embryology* - J. W. Jenkinson, *Vertebrate Embryology* - W. Patten, *The Evolution of the Vertebrates and their Kin* **(E. S. Russell).** — J. G. Frazer, *Psyche's Task. A discourse concerning the influence of superstition on the growth of institutions* - J. G. Frazer, *The Scapegoat* - J. G. Frazer, *Balder the Beautiful. The Fire-festivals of Europe and the Doctrine of the external Soul* **(L. Limentani).** — V. Tangorra, *Trattato di scienza della finanza* - E. R. A. Seligman, *The income tax* **(U. Ricci).** — M. Caudel, *Nos libertés politiques* **(G. Bourgin).**

Rivista delle Riviste - Revue des Revues - Zeitschr. Umschau - Review of Reviews.

Cronaca - Chronique - Chronik - Chronicle: *(Nouvelles diverses).*

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Articles déjà publiés par "SCIENTIA,,.

I.ère Série, fondée et dirigée par MM.:

G. Bruni - A. Dionisi - F. Enriques - A. Giardina - E. Rignano

Abegg, R. (*Breslau*): Chemische Affinität, Valenz und das natürliche System der Elemente (L'affinité chimique, la valence et le système naturel des éléments). – **1910**, n. **3.**

Abraham, M. (*Milano*): Die neue Mechanik (La nouvelle mécanique). – **1914**, n. **1.**

Acqua, C. (*Roma*): Esistono fenomeni psicologici nei vegetali? (Existe-t-il des phénomènes psychologiques dans les végétaux?). – **1914**, n. **2.**

Adler, A. (*Wien*): Die Individualpsychologie, ihre Voraussetzungen und Ergebnisse (La psychologie individuelle, ses hypothèses et ses résultats). – **1914**, n. **4.**

André, Ch. (*Lyon*): L'hypothèse nébulaire de Laplace et la théorie de la capture de M. T. J. J. See. – **1912**, n. **2.**

Arrhenius, S. (*Stockholm*): Die Unendlichkeit der Welt (L'univers infini). – **1909**, n. **2.**

— Ueber den Ursprung des Gestirnkultus (Sur l'origine du culte des astres). – **1911**, n. **2.**

— Das Milchstrassenproblem (Le problème de la Voie Lactée). – **1914**, n. **3.**

Asher, L. (*Bern*): Die Beziehungen zwischen Struktur und Funktion im tierischen Organismus (Les relations de la structure et la fonction dans l'organisme animal). – **1909**, n. **1.**

Bayliss, W. M. (*London*): The functions of enzymes in vital processes (Les fonctions des enzymes dans les processus vitaux). – **1910**, n. **4.**

Becher, S. (*Giessen*): Ueber Handlungsreaktionen und ihre Bedeutung für das Verständnis der organischen Zweckmässigkeit (Sur les réactions-actes et leur signification pour l'intelligence de la finalité organique). – **1910**, n. **4.**

Bethe, A. (*Strassburg*): Neuere Vorstellungen über die Natur der bio-elektrischen Ströme (Les idées modernes sur la nature des courants bio-électriques). – **1910**, n. **3.**

Bohlin, K. (*Stockholm*): Was ist die Milchstrasse? (Qu'est-ce que la voie lactée?). – **1910**, n. **4.**

— Die veränderlichen Sterne (Les étoiles variables). – **1912**, n. **4.**

Bohn, G. (*Paris*): Le psychisme chez les animaux inférieurs. – **1909**, n. **1.**

Bonar, J. (*Ottawa - Canada*): Home trade and foreign trade (Commerce intérieur et commerce international). – **1908**, n. **4.**

Bonnesen, T. (*Kopenhagen*): La réforme de l'enseignement des mathématiques élémentaires. – – **1907**, n. **4.**

Borel, E. (*Paris*): Le continu mathématique et le continu physique. – **1909**, n. **3.**

Bortkiewicz, L. (*Berlin*): Die statistischen Generalisationen (Les généralisations statistiques). – **1909**, n. **1.**

Boruttau, H. (*Berlin*): Die innere Sekretion (La sécrétion interne). – **1908**, n. **3.**

Bottazzi, F. (*Napoli*): La chimica fisica e la fisiologia (Chimie physique et physiologie). – **1909**, n. **4.**

— Le attività fisiologiche fondamentali. Primo articolo: L'attività nervosa e i processi elementari su cui si fonda (Les activités physiologiques fondamentales. Premier article: L'activité nerveuse et les processus élémentaires qui lui servent de base). – **1914**, n. **3.**

Bouasse, H. (*Toulouse*): Développement historique des théories de la physique. – **1910**, n. **2**.

Boutroux, P. (*Poitiers*): L'évolution des mathématiques pures. – **1909**, n. **3**.

Brillouin, M. (*Paris*): Propos sceptiques au sujet du principe de relativité. – **1913**, n. **1**.

Brunhes, B. (*Clermont-Ferrand*): La diversité de fortune des deux principes de la thermodynamique. – **1910**, n. **1**.

Bruni, G. (*Padova*): Le soluzioni solide (Les solutions solides). – **1908**, n. **3**.

— La chimica fisica nei suoi rapporti con le scienze biologiche (La chimie physique dans ses rapports avec les sciences biologiques). – **1909**, n. **3**.

— L'opera di J. H. van't Hoff (L'œuvre de J. H. van't Hoff). – **1911**, n. **3**.

Bryan, G. H. (*Bangor*): Diffusion and dissipation of energy (Diffusion et dissipation de l'énergie). – **1909**, n. **1** et **2**.

Bugge, G. (*Frankfurt a. M.*): Physikalische Eigenschaften und chemische Konstitution (Propriétés physiques et constitution chimique). – **1914**, n. **6**.

Caetani, L. (*Roma*): La funzione dell'Islàm nella evoluzione della civiltà (La fonction de l'Islam dans l'évolution de la civilisation). – **1912**, n. **3**.

Cardinali, G. (*Bologna*): Le ripercussioni dell'imperialismo sulla vita interna di Roma (Les répercussions de l'impérialisme sur la vie intérieure de Rome). – **1913**, n. **3**.

— Roma e la civiltà ellenistica (Rome et la civilisation hellénique). – **1913**, n. **4**.

Carver, T. N. (*Cambridge - U. S. A.*): The english classical school of political economy (L'école classique anglaise d'économie politique). – **1907**, n. **2**.

— Diminishing returns and value (Diminution du rendement et de la valeur). – **1909**, n. **4**.

Castelnuovo, G. (*Roma*): Il valore didattico della matematica e della fisica (La valeur didactique des mathématiques et de la physique). – **1907**, n. **2**.

— Il principio di relatività e i fenomeni ottici (Le principe de relativité et les phénomènes optiques). – **1911**, n. **1**.

Caullery, M. (*Paris*): La méthode et les critères de la morphologie. – **1908**, n. **3**.

Celoria G. (*Milano*): L'opera di Giovanni Schiaparelli (L'œuvre de Giovanni Schiaparelli). – – **1911**, n. **2**.

Chamberlin, T. C. (*Chicago*): The planetesimal hypothesis (L'hypothèse planétésimale). – **1914**, n. **5**.

Chwolson, O. (*Pétrograd*): Dürfen wir die physikalischen Gesetze auf das Universum anwenden? (Peut-on appliquer les lois de la physique à l'Univers?). – **1910**, n. **3**.

Ciamician, G. (*Bologna*): Problemi e metodi della chimica organica (Problèmes et méthodes de la chimie organique). – **1907**, n. **1**.

— La fotochimica dell'avvenire (La photochimie de l'avenir). – **1912**, n. **6**.

Claparède, E. (*Genève*): La fonction du sommeil – **1907**, n. **3**.

Costantin, J. (*Paris*): Les progrès de la culture des fleurs et leur importance pour les théories transformistes. – **1911**, n. **3**.

Crommelin, A. C. D. (*Greenwich*): The origin and nature of comets (Origine et nature des comètes). – **1910**, n. **2**.

Cuénot, L. (*Nancy*): Théorie de la préadaptation. – **1914**, n. **4**.

Cunningham, W. (*Cambridge - England*): Impartiality in history (L'impartialité de l'historien). – **1907**, n. **1**.

Darwin, G. H. (*Cambridge - England*): The rigidity of the earth (La rigidité de la Terre). – **1901**, n. **2**.

De Boissoudy, J. (*Clermont-Ferrand*): Le problème de la constitution de l'atome. – **1911**, n. **4**.

Delage, Y. (*Paris*): La parthénogénèse expérimentale et les propriétés des solutions électrolytiques. – **1907**, n. **3**.

De Marchi, L. (*Padova*): Che cos'è la Terra? (Qu'est-ce que la Terre?). – **1907**, n. **2**.

— Teorie geologiche: come si formano le montagne (Théories géologiques: comment se forment les montagnes). – **1909**, n. **4**.

De Marchi, L (*Padova*): Nuove teorie sulle cause dell'era glaciale (Nouvelles théories relatives aux causes de l'ère glaciaire). – **1911**, n. **2**.

De Martonne, E. (*Paris*): Le climat facteur du relief. – **1913**, n. **3**.

Demoor, J. (*Bruxelles*): A propos du mécanisme des phénomènes d'irritabilité. – **1909**, n. **3**.

Deonna, W. (*Genève*): Qu'est-ce que l'archéologie? – **1914**, n. **6**.

Dionisi, A. (*Modena*): Il concetto di malattia (Le concept de maladie). – **1908**, n. **2**.

Doelter, C. (*Wien*): Die Anwendung der physikalischen Chemie auf Mineralogie und Geologie (La chimie physique appliquée à la minéralogie et à la géologie). – **1908**, n. **1**.

Driesch, H. (*Heidelberg*): Die Physiologie der individuellen organischen Formbildung (La physiologie du développement de la forme organique individuelle). – **1907**, n. **2**.

Durkheim, E. (*Paris*): Le dualisme de la nature humaine et ses conditions sociales. – **1914**, n. **2**.

Dussaud, R. (*Paris*): Le rôle des Phéniciens dans la Méditerranée primitive. – **1913**, n. **1**.

Ebstein, W. (*Göttingen*): Zur Geschichte der Entwicklung des Krankheitsbegriffes (Pour l'histoire du concept de maladie). – **1908**, n. **1**.

Eddington, A. S. (*Greenwich*): Star-Streams (Les courants stellaires). – **1910**, n. **3**.

Edgeworth, F. Y. (*Oxford*): On the use of differential calculus in economics (De l'usage du calcul différentiel en économie politique). – **1910**, n. **1**.

Einhorn, D. (*Lemberg*): Archigonie und Deszendenztheorie (Archigonie et théorie de la descendance). – **1914**, n. **5**.

Einstein, A. (*Zürich*): Zum Relativitätsproblem (Sur le problème de la relativité). – **1914**, n. **3**.

Emery, C. (*Bologna*): Il polimorfismo e la fondazione delle società negli insetti sociali (Le polymorphisme et la fondation des sociétés chez les insectes sociaux). – **1910**, n. **2**.

— Le piante formicarie (Les plantes à fourmis). – **1912**, n. **4**.

Engelmeyer, P. K. (*Moscou*): Heurologischer Wert der technischen Erfindung (La valeur heurologique de l'invention technique). – **1911**, n. **3**.

Enriques, F. (*Bologna*): Heterodox science and its social function (La science hétérodoxe et sa fonction sociale). – **1907**, n. **2**.

— Le principe d'inertie et les dynamiques non-newtoniennes. – **1907**, n. **3**.

— L'università italiana (L'université italienne). – **1908**, n. **1**.

— La riforma dell'università italiana (La reforme de l'université italienne). – **1908**, n. **2**.

— Il principio di ragion sufficiente nella costruzione scientifica (Le principe de raison suffisante dans la construction scientifique). – **1909**, n. **1**.

— Razionalismo e storicismo (Rationalisme et historisme). – **1909**, n. **2**.

— La teoria dello Stato e il sistema rappresentativo (La théorie de l'État et le système représentatif). – **1909**, n. **3**.

— La filosofia positiva e la classificazione delle scienze (La philosophie positive et la classification des sciences). – **1910**, n. **2**.

— Il pragmatismo (Le pragmatisme). – **1910**, n. **3**.

— I numeri e l'infinito (Les nombres et l'infini). – **1911**, n. **1**.

— Il problema della realtà (Le problème de la réalité). – **1911**, n. **2**.

— Matematiche e teoria della conoscenza (Mathématiques et théorie de la connaissance). – **1912**, n. **1**.

— Il significato della critica dei principii nello sviluppo delle matematiche (La critique des principes et son rôle dans le développement des mathématiques). – **1912**, n. **5**.

Enriques, P. (*Bologna*): La morte (La mort). – **1907**, n. **3**.

— — — — et **Gortani,** M. (*Bologna*): La successione degli strati e la teoria dei periodi geologici (La succession des couches et la théorie des périodes géologiques). – **1909**, n. **4**.

Fabry, Ch. (*Marseille*): La théorie électromagnétique de l'univers. – **1907**, n. **4** et **1908**, n. **1**

Fano, Gino (*Torino*): La geometria non-euclidea (La géométrie non-euclidienne). – **1908**, n. **4**.

Fano, Giulio (*Firenze*): Chimica e biologia (Chimie et biologie). – **1907**, n. **4**.

Findlay, Alex. (*Aberystwith*): Osmotic pressure and the theory of solutions (La pression osmotique et la théorie des solutions). – **1912**, n. **4**.

— Heterogeneous equilibrium and the phase rule (L'équilibre hétérogène et la loi des phases). – **1913**, n. **4**.

Fisher, I. (*New Haven, Conn. – U. S. A.*): The « impatience » theory of interest (Une théorie de l'intérêt fondée sur l'impatience). – **1911**, n. **2**.

Foà, P. (*Torino*): Il significato biologico dei tumori (La signification biologique des tumeurs) – **1908**, n. **1**.

Fournier d'Albe, E. E. (*Birmingham*): Interstellar space (L'espace interstellaire). – **1913**, n **4**.

Fowler, A. (*London*): The chemical unity of the cosmos (L'unité chimique du monde). – **1911**, n. **4**.

Francé, R. H. (*München*): Das Reaktionsvermögen der Pflanze (Le pouvoir de réaction des plantes). – **1909**, n. **4**.

Fredericq, L. (*Liège*): De la coordination organique par action chimique. – **1909**, n. **2**.

— Les moyens de défense physiques et chimiques dans le règne animal. – **1913**, n. **4**.

Freud, S. (*Wien*): Das Interesse an der Psychoanalyse. I. Teil: Das psychologische Interesse (L'intérêt de la psycho-analyse. Ière Partie: Son intérêt pour la psychologie). – **1913**, **n. 5**.

— Das Interesse an der Psychoanalyse. II. Teil: Ihr Interesse für die anderen Wissenschaften (L'intérêt de la psycho-analyse. IIème Partie: Son intérêt pour les autres sciences). – **1913**, n. **6**.

Galeotti, G. (*Napoli*): Le teorie sulla immunità (Les théories sur l'immunité). – **1910**, n. **1**.

— La dottrina degli anticorpi (L'état de nos connaissances sur les anticorps). – **1910**, n. **2**.

Gini, C. (*Bologna*): Che cos'è la probabilità? (Qu'est-ce que la probabilité?) – **1908**, n. **2**.

Giuffrida-Ruggeri, V. (*Napoli*): Il pithecanthropus erectus e l'origine della specie umana (Le pithecanthropus erectus et l'origine de l'espèce humaine). – **1907**, n. **4**.

Goblot, E. (*Lyon*): Le concept et l'idée. – **1912**, n. **1**.

Golgi, C. (*Pavia*): La moderna evoluzione delle dottrine e delle conoscenze sulla vita. Parte I: I problemi fondamentali bio-fisiologici (L'évolution moderne des doctrines et des connaissances sur la vie. Ière Partie: Les problèmes fondamentaux bio-physiologiques). – **1914**, n. **5**.

— La moderna evoluzione delle dottrine e delle conoscenze sulla vita. Parte II: I problemi fondamentali psico-fisiologici (L'évolution moderne des doctrines et des connaissances sur la vie, IIème Partie: Les problèmes fondamentaux psycho-physiologiques). – **1914**, n. **6**.

Grammont, M. (*Montpellier*): Phonétique historique et phonétique expérimentale. – **1912**, n. **4**.

Gregory, J. W. (*Glasgow*): The structural and petrographic classifications of coast-types (Les classifications structurelle et pétrographique des types des côtes). – **1912**, n. **1**.

Guignebert, Ch. (*Paris*): Les origines chrétiennes. – **1910**, n. **3**.

— L'évolution du christianisme ancien. – **1910**, n. **4**.

— De Saint Augustin à Pie X. – **1911**, n. **1**.

— Le dogme de la Trinité. Ière Partie: Les triades primitives et la formule baptismale. – **1913**, n. **6**.

— Le dogme de la Trinité. IIème Partie: L'évolution des deux triades et les premiers conflits. – **1914**, n. **1**.

— Le dogme de la Trinité. IIIème Partie: La crise arienne, S. Augustin et le symbole d'Athanase. IVème Partie: Immobilité, décadence et ruine. – **1914**, n. **5**.

Günther, S. (*München*): Pseudo- und kryptovulkanische Erdbeben (Tremblement de Terre pseudo- et crypto-volcaniques). – **1913**, n. **4**.

Haberlandt, G. (*Graz*): Ueber Bewegung und Empfindung im Pflanzenreich (Du mouvement et de la sensibilité dans le règne végétal). – **1908**, n. **2**.

Hahn, E. (*Berlin*): Die Entstehung der Bodenwirtschaft (Les origines de l'économie agricole). – **1911**, n. **1**.

Hartog, M. (*Cork*): The dynamics of mitotic celldivision (La dynamique de la division cellulaire mitotique). – **1907**, n. **3**.

— Samuel Butler and recent mnemic biological theories (Samuel Butler et les récentes théories biologiques de la mémoire). – **1914**, n. **1**.

Henslow, G. (*Bournemouth*): Ecology considered as bearing upon the evolution of plants (L'écologie au point de vue de l'évolution des végétaux). – **1913**, n. **2**.

Herbertson, A. J. (*Oxford*): The higher units. A geographical essay (Les unités supérieures. Essai géographique). – **1913**, n. **5**.

Hertwig, O. (*Berlin*): Disharmonische Idioplasmaverbindungen und ihre Folgen (Fusions disharmoniques de l'idioplasma et leurs produits). – **1912**, n. **6**.

Herz, N. (*Wien*): Die Eiszeiten (Les époques glaciaires). – **1911**, n. **1**.

— Philosophische Konzeption und mathematische Analyse in der Weltbetrachtung (Conception philosophique et analyse mathématique dans l'observation de l'Univers). – **1911**, n. **3**.

— Die Entwicklung der Erde (L'évolution de la Terre). – **1912**, n. **2**.

Hinks, A. R. (*Cambridge*): The measurement of celestial distances (La mensuration des distances célestes). – **1912**, n. **3**.

Höber, R. (*Kiel*): Die biologische Bedeutung der Kolloide (La valeur biologique des colloïdes). – **1910**, n. **1**.

Hoernes, Moriz (*Wien*): Die körperlichen Grundlagen der Kulturentwicklung (Les bases structurales du développement intellectuel). – **1910**, n. **2**.

— Die ältesten Formen der menschlichen Behausung und ihr Zusammenhang mit der allgemeinen Kulturentwicklung (Les plus anciennes formes de l'habitation humaine et leur relation avec le développement général de la civilisation). – **1911**, n. **3**.

— Ursprung und älteste Formen der menschlichen Bekleidung (Origine et formes les plus anciennes du vêtement humain). – **1912**, n. **1**.

Hoernes, Rudolf (*Graz*): Die Bedeutung der Paläontologie für die Erdgeschichte (La signification de la paléontologie pour l'histoire de la Terre). – **1911**, n. **4**.

Jacobi, H. (*Bonn*): Was ist Sanskrit? (Qu'est-ce que le sanscrit?). – **1913**, n. **5**.

Janet, P. (*Paris*): Le subconscient. – **1910**, n. **4**.

Jespersen, O. (*Gentofte - Danemark*): Origin of linguistic species (L'origine des espèces linguistiques). – **1909**, n. **3**.

— Energetik der Sprache (L'énergétique du langage). – **1914**, n. **5**.

Kapteyn, J. C. (*Groningen*): On the structure of the universe (Sur la structure de l'univers). – **1913**, n. **6**.

Kidd, B. (*Oxford*): The two capital laws of sociology (Les deux lois fondamentales de la sociologie). – **1907**, n. **4** et **1908**, n. **1**.

Kühnert, F. (*Wien*): Die ideographische Schrift und ihre Beziehung zum Sprachbau im Chinesischen (L'écriture idéographique et les rapports avec la formation de la langue dans le chinois). – **1913**, n. **1**.

Landry, A. (*Paris*): Les trois théories principales de la population. – **1909**, n. **3**.

— L'école économique autrichienne. – **1907**, n. **3** et **4**.

Langdon, S. (*Oxford*): Babylonian magic (La magie babylonienne). – **1914**, n. **2**.

Langevin, P. (*Paris*): L'évolution de l'espace et du temps. – **1911**, n. **3**.

Lebedew, P. (*Moscou*): Die Druckkräfte des Lichtes (Les forces de pression de la lumière). – **1910**, n. **2**.

Le Dantec, F. (*Paris*): Comment se pose la question de l'hérédité des caractères acquis. – **1908**, n. **4**.

Lehmann, O. (*Karlsruhe*): Scheinbar lebende fliessende Kristalle; künstliche Zellen und Muskeln (Cristaux fluides ayant une apparence de vie organique; cellules et muscles artificiels). – **1908**, n. **4**.

Levi, A. (*Firenze*): Il pensiero scientifico europeo nel secolo decimonono (La pensée scientifique en Europe au XIX siècle). – **1908**, n. **4**.

Loisy, A. (*Paris*): La critique des évangiles. – **1910**, n. **4**.

Lorentz, H. A. (*Haarlem*): La gravitation. – **1914**, n. **4**.

Loria, A. (*Torino*): L'indirizzo storico nella scienza economica (Le point de vue historique dans la science économique). – **1908**, n. **1**.

Lowell, P. (*Flagstaff, Arizona - U. S. A.*): Mars (Mars). – **1910**, n. **1**.

Lugaro, E. (*Modena*): Preformismo ed epigenesi nello sviluppo del sistema nervoso (Préformisme et épigénèse dans le développement du système nerveux). – **1910**, n. **2**.

Mach, E. (*Wien*): Die Leitgedanken meiner naturwissenschaftlichen Erkenntnislehre und ihre Aufnahme durch die Zeitgenossen (Les idées directrices de ma théorie de la connaissance dans les sciences naturelles et l'accueil qu'elles ont reçu des contemporains). – **1910**, n. **2**.

Maunder, E. W. (*Greenwich*): The « canals » of Mars (Les « canaux » de Mars). – **1910**, n. **2**.

— The Sun-Spots (Les taches du Soleil). – **1913**, n. **1**.

Maunier, R. (*Paris*): La sociologie française contemporaine. – **1910**, n. **3**.

Mazzarella, G. (*Catania*): L'etnologia giuridica, i suoi metodi, i suoi risultati (L'ethnologie juridique, ses méthodes, ses résultats). – **1910**, n. **3**.

Mecklenburg, W. (*Klausthal i. H.*): Die Lehre von den Elektrolytlösungen (La théorie des solutions électrolytiques). – **1913**, n. **6**.

Meillet, A. (*Paris*): Linguistique historique et linguistique générale. – **1908**, n. **4**.

— Différenciation et unification dans les langues. – **1911**, n. **2**.

— L'évolution des formes grammaticales. – **1912**, n. **6**.

— Le problème de la parenté des langues. – **1914**, n. **3**.

Miceli, V. (*Palermo*): Gli elementi vivi del diritto (Les éléments vivants du droit). – **1910**, n. **4**.

Michels, R. (*Torino*): Economia e politica (Économie et politique). – **1914**, n. **3**.

Mieli, A. (*Roma*): Le teorie delle sostanze nei presocratici greci. I[a] Parte: Dalle prime speculazioni fino ad Empedocle (Les théories des substances chez les présocratiques grecs. Ière Partie: Des premières spéculations à Empédocle). – **1913**, n. **5**.

— Le teorie delle sostanze nei presocratici greci. II[a] Parte: Anassagora e gli atomisti (Les théories des substances chez les présocratiques grecs. IIème Partie: Anaxagore et les atomistes). – **1913**, n. **6**.

Milhaud, G. (*Montpellier*): Cournot et le pragmatisme scientifique contemporain. – **1911**, n. **4**.

Millosevich, E. (*Roma*): Dalla torre di Babele al laboratorio di Groninga (De la tour de Babel au laboratoire de Groningue). – **1912**, n. **5**.

Moreux, Th. (*Bourges*): Le Soleil et la prévision des pluies. – **1910**, n. **4**.

— Où nous entraîne notre Soleil? – **1913**, n. **5**.

Naville, E. (*Genève*): La méthode scolastique dans la science du langage. – **1913**, n. **2**.

Nernst, W. (*Berlin*): Sur quelques nouveaux problèmes de la théorie de la chaleur. – **1911**, n. **4**.

Oppenheimer, F. (*Berlin*): Wesen und Entstehung des Kapitalismus (L'essence et l'origine du capitalisme). – **1908**, n. **2** et **4**.

— Wert und Mehrwert. I. Teil: Die Monopol-Theorie des Mehrwertes (Valeur et plus-value. Ière Partie: La théorie de monopole de la plus-value). – **1913**, n. **2**.

— Wert und Mehrwert. II. Teil: Kritik der Marx'sche Theorie des Mehrwertes (Valeur et plus-value. IIème Partie: Critique de la théorie de la plus-value de Marx). – **1913**, n. **3**.

Ostwald, W. (*Leipzig*): Zur modernen Energetik (De l'énergétique moderne). – **1907**, n. **1**.

— Der Wille und seine physische Grundlegung (La volonté et sa base physique). – **1911**, n. **2**.

— Ueber Organisation und Organisatoren. I. Teil: Allgemeine Theorie (De l'organisation et des organisateurs. Ière Partie: Théorie générale). – **1912**, n. **5**.

— Ueber Organisation und Organisatoren. II. Teil: Moderne Probleme (De l'organisation et des organisateurs. IIème Partie: Problèmes modernes). – **1912**, n. **6**.

Pareto, V. (*Losanne*): L'économie et la sociologie au point de vue scientifique. – **1907**, n. **2**.

Pearl, R. (*Orono, Maine – U. S. A.*): Biometrical ideas and methods in biology: their significance and limitations (Les idées et méthodes biométriques en biologie: leur signification et leurs limitations). – **1911**, n. **3**.

Perozzi, S. (*Bologna*): Socialismo giuridico (Le socialisme juridique). – **1911**, n. **3**.

— Precetti e concetti nell'evoluzione giuridica (Préceptes et concepts dans l'évolution juridique). – **1912**, n. **3**.

Pettazzoni, R. (*Roma*): La scienza delle religioni e il suo metodo (La science des religions et sa méthode). – **1913**, n. **2**.

— Storia del cristianesimo e storia delle religioni (Histoire du christianisme et histoire des religions). – **1914**, n. **4**.

Picard, E. (*Paris*): La mécanique classique et ses approximations successives. – **1907**, n. **1**.

Piéron, H. (*Paris*): Le problème de l'orientation. envisagé chez les fourmis. – **1912**, n. **5**.

Pikler, J. (*Budapest*): Ueber die biologische Funktion des Bewusstseins (Sur la fonction biologique de la conscience). – **1909**, n. **2**.

Pizzetti, P. (*Pisa*): Le misurazioni fisiche e la teoria degli errori d'osservazione (Les mesurages physiques et la théorie des erreurs d'observation). – **1907**, n. **3**.

Poincaré, H. (*Paris*): L'avenir des mathématiques. – **1908**, n. **3**.

— L'évolution des lois. – **1911**, n. **2**.

— La logique de l'infini. – **1912**, n. **4**.

— L'espace et le temps. – **1912**, n. **5**.

Prenant, A. (*Paris*): Les théories physiques de la mitose. – **1913**, n. **3**.

Pringsheim, E. (*Breslau*): Temperaturstrahlung und Lumineszenz (Rayonnement thermique et luminescence). – **1913**, n. **2**.

Puiseux, P. (*Paris*): La place du Soleil parmi les étoiles. – **1911**, n. **1**.

Rabaud, E. (*Paris*): L'évolution tératologique. – **1911**, n. **1**.

Raffaele, F. (*Palermo*): Il concetto di specie in biologia: I. Avanti e in Darwin; II. La critica post-darviniana (Le concept d'espèce en biologie: I. Avant et chez Darwin; II. La critique post-darwinienne). – **1907**, n. **1** et **2**.

Reinach, S. (*Paris*): De l'influence des images sur la formation des mythes. – **1909**, n. **2**.

Rey, A. (*Paris*): La possibilité d'une méthode positive dans la théorie de la connaissance. – **1909**, n. **4**.

— L'ostracisme du concept de force dans la physique moderne. – **1912**, n. **3**.

Riccobono, S. (*Palermo*): L'influenza del cristianesimo nella codificazione di Giustiniano (L'influence du christianisme dans la codification de Justinien). – **1909**, n. **1**.

Rignano, E. (*Milano*): Le rôle des « théoriciens » dans les sciences biologiques et sociologiques. – **1912**, n. **2**.

— La mémoire biologique en énergétique. – **1909**, n. **3**.

— Dell'origine e natura mnemonica delle tendenze affettive (De l'origine et de la nature mnémonique des tendances affectives). – **1911**, n. **1**.

— Dell'attenzione. Iª Parte: Contrasto affettivo e unità di coscienza (De l'attention. Ière Partie: Contraste affectif et unité de conscience). – **1911**, n. **4**.

— Dell'attenzione. IIª Parte: Vividità e connessione (De l'attention. IIème Partie: Vividité et connexion). – **1912**, n. **1**.

— Che cos'è il ragionamento? (Qu'est-ce que le raisonnement?). – **1913**, n. **1**.

— L'evoluzione del ragionamento. Iª Parte: Dal ragionamento concreto al ragionamento astratto (L'évolution du raisonnement. Ière Partie: Du raisonnement concret au raisonnement abstrait). – **1913**, n. **4**.

— L'evoluzione del ragionamento. IIª Parte: Dall'intuizione alla deduzione (L'évolution du raisonnement. IIème Partie: De l'intuition à la déduction). – **1913**, n. **5**.

— Qu'est-ce que la conscience? – **1907**, n. **4**.

— Il fenomeno religioso (Le phénomène religieux). – **1910**, n. **1**.

— Le matérialisme historique. – **1908**, n. **3**.

— Il socialismo (Le socialisme). – **1910**, n. **4**.

Righi, A. (*Bologna*): Comete ed elettroni (Comètes et électrons). – **1910**, n. **4**.

— La natura dei raggi X (La nature des rayons X). – **1914**, n. **1**.

Ritz, W. (*Göttingen*): Die Gravitation (La gravitation). – **1909**, n. **2**.

— Du rôle de l'éther en physique. – **1908**, n. **2**.

Rosa, D. (*Firenze*): Delle leggi che regolano la variabilità filogenetica (Des lois qui gouvernent la variabilité phylogénétique). – **1908**, n. **4**.

— I dilemmi fondamentali circa il metodo dell'evoluzione (Dilemmes fondamentaux touchant la méthode de l'évolution). – **1912**, n. **2**.

Rouse, W. H. D. (*Cambridge*): Classical work and method in the twentieth century (Les études classiques pendant le XX^{e} siècle). – **1908**, n. **3**.

Rudzki, M. P. (*Cracovie*): L'âge de la Terre. – **1913**, n. **2**.

Russell, B. (*Cambridge*): On the notion of cause (Sur la notion de cause). – **1913**, n. **3**.

— The relation of sense-data to physics (Les rapports des données sensorielles avec la physique). – **1914**, n. **4**.

Russell, E. S. (*London*): The evidence of natural selection (Les preuves de l'existence d'une sélection naturelle). – **1909**, n. **1**.

— Vitalism (Le vitalisme). – **1911**, n. **2**.

Rutherford, E. (*Manchester*): The structure of the atom (La structure de l'atome). – **1914**, n. **6**.

Sagnac, Ph. (*Lille*): De l'importance relative des faits économiques dans l'évolution historique. – **1909**, n. **2**.

— L'esprit et les progrès de la Révolution Française: Ière Partie: Les origines de la Révolution. – **1914**, n. **1**.

Sayce, A. H. (*Oxford*): The laws of Babylonia (Les lois de Babylone). – **1912**, n. **1**.

Schiaparelli, G. (*Milano*): I primordi dell'astronomia presso i Babilonesi (La naissance de l'astronomie chez les Babyloniens). – **1908**, n. **2**.

— I progressi dell'astronomia presso i Babilonesi (Les progrès de l'astronomie chez les Babyloniens). – **1908**, n. **3**.

Scialoja, V. (*Roma*): L'arbitrio del legislatore nella formazione del diritto positivo (L'arbitraire du législateur dans la formation du droit positif). – **1910**, n. **1**.

Scott, D. H. (*London*): The evolution of plants (L'évolution des plantes). – **1912**, n. **5**.

See, T. J. J. (*Mare Island, California – U. S. A.*): The new science of cosmogony (La nouvelle science de la cosmogonie). – **1912**, n. **1**.

— The law of nature in celestial evolution (La loi de nature dans l'évolution céleste). – **1914**, n. **2**.

Seeliger, H. (*München*): Ueber die Anwendung der Naturgesetze auf das Universum (Sur l'application des lois de la nature à l'Univers). – **1909**, n. **4**.

Semon, R. (*München*): Die physiologischen Grundlagen der organischen Reproduktionsphaenomene (Les fondements physiologiques des phénomènes organiques de reproduction). – **1910**, n. **2**.

Sergi, G. (*Roma*): Lacune nella scienza antropologica (Quelques lacunes dans la science anthropologique). – **1909**, n. **3**.

Severi, F. (*Padova*): Ipotesi e realtà nelle scienze geometriche (Hypothèses et réalité dans les sciences géométriques). – **1910**, n. **3**.

Sherrington, Ch. S. (*Liverpool*): The « rôle » of reflex inhibition (Le rôle de l'inhibition réflexe). – **1911**, n. **2**.

Simmel, G. (*Berlin*): Beiträge zur Philosophie der Geschichte (Quelques considérations sur la philosophie de l'histoire). – **1909**, n. **4**.

Smoluchowski, M. (*Lemberg*): Anzahl und Grösse der Moleküle und Atome (Nombre et dimensions des molécules et des atomes). – **1913**, n. **1**.

Soddy, F. (*Glasgow*): The parent of radium (Le père du radium). – **1909**, n. 2.

— Transmutation, the vital problem of the future (La transmutation, problème vital de l'avenir). – **1912**, n. **2**.

— The periodic law from the standpoint of radioactivity (La loi des périodes envisagée au point de vue de la radioactivité). – **1913**, n. **3**.

Solla, R. (*Pola*): Die Pflanzenphysiologie in ihren Beziehungen zu den anderen Wissenschaften (La physiologie végétale et ses rapports avec les autres sciences). – **1907**, n. **2**.

Sollas, W. J. (*Oxford*): The evolution of man (L'évolution de l'homme). – **1911**, n. **1**.

Sombart, W. (*Breslau*): Die Entstehung der Städte im Mittelalter (L'origine des villes au moyen âge). – **1907**, n. **3**.

— Judaismus und Kapitalismus (Judaïsme et capitalisme). – **1912**, n. **3**.

— Liebe, Luxus und Kapitalismus (Amour, luxe et capitalisme). – **1914**, n. **2**.

Sommerfeldt, E. (*Tübingen*): Grundlagen der theoretischen Kristallographie (Les bases de la cristallographie théorique). – **1907**, n. **3**.

Suali, L. (*Pavia*): Esiste una filologia indiana? (Existe-t-il une philologie indienne?) – **1911**, n. **4**.

Suess, F. E. (*Wien*): Moderne Theorien der Erdbeben und Vulkane (Les théories modernes sur les tremblements de terre et les volcans). – **1909**, n. **3** et **4**.

Supino, C. (*Pavia*): Il carattere delle leggi economiche (Le caractère des lois économiques). – **1907**, n. **1**.

Tannery, J. (*Paris*): Questions pédagogiques: L'enseignement secondaire. – **1907**, n. **1**.

Thomson, A. (*Aberdeen*): What determines sex? (Qu'est-ce qui détermine le sexe?). – **1912**, n. **3**.

— Sex-characters (Les caractères sexuels). – **1914**, n. **3**.

Turner, H. H. (*Oxford*): The periodicities of Sun-Spots (La périodicité des taches solaires). – **1914**, n. **1**.

Uexküll, J. v. (*Heidelberg*): Die neuen Fragen in der experimentellen Biologie (Nouvelles questions de la biologie expérimentale). – **1908**, n. **3**.

Vacca, G. (*Roma*): La scienza nell'Estremo Oriente (La science dans l'Extrême-Orient). – **1912**, n. **2**.

Volterra, V. (*Roma*): Il momento scientifico presente e la nuova Società italiana per il progresso delle scienze (Le moment scientifique présent et la nouvelle Société italienne pour l'avancement des sciences). – **1907**, n. **4**.

Walden, L. (*Riga*): Ueber das Wesen des Lösungsvorganges und die Rolle des Mediums (Sur la nature du processus de solution et le rôle du solvant). – **1907**, n. **4**.

Wallerant, F. (*Paris*): Les liquides cristallisés. – **1907**, n. **2**.

Westermarck, E. (*Helsingfors*): The origin of religious celibacy (Les origines du célibat religieux). – **1907**, n. **4**.

White, W. H. (*London*): The place of mathematics in engineering practice (La place des mathématiques dans la pratique du génie). – **1912**, n. **6**.

Wiesner, J. (*Wien*): Der Lichtbedarf der Pflanze (La quantité de lumière nécessaire à la plante). – **1907**, n. **4**.

Xénopol, A. D. (*Jassy*): L'idée de loi scientifique et l'histoire. – **1912**, n. **6**.

Zeeman, P. (*Amsterdam*): L'origine des couleurs du spectre. – **1909**, n. **1**.

Zeuthen, G. H. (*Kopenhagen*): Quelques traits de la propagation de la science de génération en génération. – **1909**, n. **1**.

Ziegler, H. E. (*Jena*): Die natürliche Zuchtwahl (La sélection naturelle). – **1907**, n. **1**.

Ziehen, H. (*Frankfurt a. M.*): Die Kultur der Gegenwart (La culture intellectuelle de notre temps). – **1910**, n. **1**.

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Sommaires des numéros parus en 1915 (9ème année)

Première Livraison — Janvier.

A. C. D. Crommelin - *The capture theory of satellites.* — E. Rignano - *Le forme superiori del ragionamento. Parte Ia: Il ragionamento matematico nelle sue fasi del simbolismo diretto e indiretto.*

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Deuxième Livraison — Février.

J. Costantin - *Les lois de l'hybridation et l'action du milieu.* — E. Rignano - *Le forme superiori del ragionamento. Parte IIa: Il ragionamento matematico nelle sue fasi di condensazione ed inversione simbolica.*

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Troisième Livraison — Mars.

F. Frech - *Die Salzseen Anatoliens und ihre Bedeutung für das Problem der Entstehung der Salzstöcke der Erdrinde.* — E. Rignano - *Le forme superiori del ragionamento. Parte IIIa: Matematiche e logica matematica.*

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Quatrième Livraison — Avril.

A. Mieli - *La posizione di Lavoisier nella storia della chimica.* — J. W. Gregory - *The reported progressive desiccation of the Earth.*

N. Kostyleff - *Les facteurs psychologiques de la guerre actuelle.* — L. M. Hartmann - *Ueber die Ursachen des Weltkrieges.* — Lujo Brentano - *Die letzten Ursachen des gegenwärtigen Krieges.*

Cinquième Livraison — Mai.

M. P. Rudzki - *Les théories les plus récentes sur l'origine des continents.* — E. Carnevale - *Democrazia e giustizia penale. Parte Ia: Democrazia e attitudine mentale al giudizio.*

P. Vinogradoff - *The causes of the War.* — J. Andrassy - *Weltkrieg und Weltfreiheit.* — W. L. de Jaworski - *La guerre actuelle au point de vue de la question polonaise.*

Sixième et Septième Livraison — Juin-Juillet.

G. Bohn - *Idées nouvelles sur l'adaptation et l'évolution. Ière Partie: Les désharmonies des êtres vivants.*

L. Havet - *D'une guerre à l'autre.* — J. H. Rose - *The war and nationality.* — E. Rignano - *I fattori della guerra ed il problema della pace.*

Huitième Livraison — Août.

G. Bohn - *Idées nouvelles sur l'adaptation et l'évolution. IIème Partie: Conception physico-chimique de l'évolution.* — E. Carnevale - *Democrazia e giustizia penale. Parte IIa: Democrazia, garanzie processuali, e metodi della lotta giudiziaria.*

W. J. Ashley - *The economic conversion of England.* — Ch. Guignebert - *L'Église romaine dans le conflit européen.*

Neuvième Livraison — Septembre.

G. Peano - *Importanza dei simboli in matematica.* — The. Svedberg - *Structure et formes des molécules.* — E. H. Starling - *The animal machine and its automatic regulation.*

A. Meillet - *Les langues et les nationalités.* — R. Michels - *Cittadinanza e nazionalità.*

Dixième Livraison — Octobre.

A. Mieli - *La scienza greca e le caratteristiche del suo sviluppo.* — P. Puiseux - *L'avenir des planètes.* — C. Lloyd Morgan - *Mind and body in their relations to each other and to external things.*

R. Muir - *The antipathy between Germany and England.*

Onzième Livraison — Novembre.

A. S. Eddington - *The stellar universe as a dynamical system.* — Ch. Fabry - *Les atomes lumineux et leurs mouvements. Ière Partie: Les mouvements des particules lumineuses.* — M. Vallauri - *La medicina indiana.*

P. Bonfante - *Verso la confederazione europea.*

Douzième Livraison — Décembre.

G. Loria - *L'infinito e l'infinitesimo secondo i matematici dell'antichità.* — Ch. Fabry - *Les atomes lumineux et leurs mouvements. IIème Partie: La constitution de l'atome lumineux.* — W. H. Bragg - *The new crystallography.*

R. Muir - *The problems of the future peace.* — P. Fedozzi - *Gli insegnamenti della guerra circa il trattamento degli stranieri.*

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Notes critiques - Comptes rendus - Revues générales - Revue des Revues - Chronique.

Sommaires des numéros parus en 1916 (10ème année)

Première Livraison - (N. XLV) - (Janvier 1916)

G. Loria – *L'infinito e l'infinitesimo secondo i matematici moderni anteriori al secolo XVIII – (L'infiniment grand et l'infiniment petit d'après les mathématiciens modernes antérieurs au XVIIIe siècle).*
P. Lowell – *The atmosphere of Mars – (L'atmosphère de Mars).*
H. De Vries – *L'évolution des êtres organisés, par sauts brusques.*

A. Graziani – *Le future conseguenze economiche della guerra – (Les futures conséquences économiques de la guerre).*
A. Weiss – *Le droit international d'hier et de demain.*

Comptes rendus - Revue des Revues - Chronique.

Deuxième Livraison - (N. XLVI) - (Février 1916)

Th. Moreux – *Les « Novæ » et la constitution de l'univers.*
F. Bottazzi – *Le attività fisiologiche fondamentali. Secondo Articolo: L'attività muscolare – (Les activités physiologiques fondamentales. Deuxième Article: L'activité musculaire).*
A. S. D. Maunder – *Iranian Migrations before History – (Migrations Iraniennes avant l'histoire).*

Ch. Gide – *Les dépenses de la guerre et leurs conséquences économiques.*
A. Loria – *Riflessioni e previsioni a proposito della guerra – (Réflexions et prévisions à propos de la guerre).*

Comptes rendus - Revue des Revues

Troisième Livraison - (N. XLVII) - (Mars 1916)

C. G. Abbot – *The Nature of the Sun – (La nature du Soleil).*
E. Bouty – *La théorie cinétique des gaz. Ière Partie: Ses fondements.*
L. Matruchot – *Le problème du cancer éclairé par la pathologie végétale.*

O. Jespersen – *Réflexions d'un Danois sur la guerre.*
C. Supino – *Le fonti economiche della guerra – (Les sources économiques de la guerre).*

Comptes rendus - Revue des Revues.

Quatrième Livraison - (N. XLVIII) - (Avril 1916)

A. Mieli – *Il periodo pneumatico della chimica – (La période pneumatique de la chimie).*
E. Bouty – *La théorie cinétique des gaz. IIème Partie: Ses progrès et ses difficultés.*
E. Rabaud – *Les phénomènes embryonnaires et la phylogénèse.*

J. H. Rose – *The Future of Europe – (L'avenir de l'Europe).*
C. A. Reuterskiöld – *Les lignes directrices du droit des gens après la guerre.*

Comptes rendus - Revues générales - Revue des Revues - Chronique.

Cinquième Livraison - (N. XLIX) - (Mai 1916)

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W. M. BAYLISS

SURFACE PHENOMENA IN LIVING STRUCTURES

If a muscle is set into activity by a stimulus and the energy of the contractile process measured by the amount of heat produced when no external work is done, it is found that this energy is directly proportional to the *length* of the fibres during the time in which the contractile stress is developed. The fact that there is a difference between the energy produced when the fibres are allowed to shorten and that produced when no change of length occurs shows at once that the *volume* of the muscle has no influence on the process, because there is no change in the volume. It is clear, therefore, that the amount of energy set free is proportional to the area of certain surfaces arranged in a longitudinal direction in the muscle. This view was first put forward by Blix, but it is the work of A. V. Hill that has shown the exact relationship between the length of the fibres and the tension developed.

Again, the experiments of Warburg, confirmed by others, have shown that alkalies exercise a powerful effect on oxidation processes in cells, even when they do not enter the cell. This action must therefore be produced by means of the outer surface of the cell.

One more case may be taken from a different set of phenomena. The activity of those catalysts which we call enzymes is now known to be exerted by the surfaces of the colloidal particles into which they are divided.

Many other illustrations might be given, but I have merely taken those referred to above in order to show at the outset the necessity for the physiologist of an intimate know-

ledge of the processes occurring at interfaces of contact between different constituents of a heterogeneous system. The more insight indeed that we obtain of the conditions present at such situations, the better position shall we be in for interpreting the complexity of vital processes.

It is obvious enough that the visible structures of an organism are composed of materials which do not mix together, but it requires the aid of the microscope to demonstrate the same fact with regard to the architecture of the cells forming the constructional units of these larger parts. Moreover, a large number of the liquids which play so important a part in the mechanism of the cell are shown by the ultramicroscope to be heterogeneous, in that they are what are called « colloidal solutions ». To use the word introduced by Willard Gibbs, we may say that living processes take place in systems of many « phases », some of these being minutely subdivided. The complexity is great and, in order to build on sure foundations, it is necessary to understand to begin with the behaviour of the simplest systems of two phases only.

Suppose then that we have such a system consisting, say, of particles of sand immersed in water. It is quite clear that the molecules of either of these phases at the interface between each other are exposed to the action of forces which differ from those to which the molecules in the interior of this phase are exposed. The latter are under the influence of forces of a similar nature on all sides; those at the surface on the contrary, are exposed on the one side to the influence of molecules similar to themselves, on the other side to molecules unlike themselves. Without any further analysis, we can see that there must be forces present at the boundaries of phases which differ from those in the interior of the phases. Now one of the forms in which this fact shows itself is the state of tension which is found to exist where a liquid is in contact with another phase, a gas, a solid, or another liquid with which the first mentioned does not mix. This surface tension was investigated by Thomas Young and has been explained by the internal pressure shown by Laplace to be present in liquids owing to the attractive force of molecules on each other. This attraction is also familiar to us in the factor a of van der Waals' equation of state. The enormous resistance shown by liquids to an increase of volume, sometimes referred to as

« cohesion », is another way in which the great force of attraction between molecules makes itself manifest. At the free surface of a liquid, its molecules are exposed to unbalanced forces of this kind, by which the constituent elements of the surface film would be drawn inwards, if it were possible. The surface film, accordingly, behaves as if stretched. The surface is thus the seat of a form of energy, of which the surface tension is the intensity factor and the area is the capacity factor.

When substances are dissolved in liquids, they lower the surface tension of these liquids, with very few exceptions, and, up to a certain limit, in proportion to their concentration therein.

Let us next call to mind what is taught us by the second law of energetics, not forgetting that this law is no more than an expression of universal experience; but, nevertheless, no exception from it has ever been found. We are therefore completely justified in concluding that what it predicts as necessary will certainly take place. One form in which this law has been expressed is in what is sometimes known as the « Principle of Carnot and Clausius », which states that free energy, that is, energy from which useful work can be obtained, always diminishes, if the conditions are such that it is able to do so. Kelvin's law of the dissipation of energy expresses the same fact. If, then, increased concentration of a solute decreases surface energy, such increase of concentration will take place at the interface between phases. The necessity of this was pointed out by Willard Gibbs and is the basis of the phenomenon known as « adsorption ». One must be very explicit as to what one means by the name, since it has been used in a loose manner and applied to any reaction in which the ordinary chemical laws of combining proportion appear to be disobeyed. Unless the use of a name implies a definite phenomenon, nothing but obstruction to the progress of science can result.

The use of charcoal to remove certain substances from solution is a common practice, but it is not always realized that the substances which seem to disappear are merely attached to the surface of the charcoal and can be removed by appropriate means. This can be shown by a simple experiment. Take a dilute solution of a socalled « basic » dye, which is strongly adsorbed, such as methylene blue. Add charcoal

until the solution is decolourized. Filter off the charcoal and extract it with absolute alcohol. The pigment will be removed from the surface and go into solution in the alcohol. The reason why it is removed by alcohol is because the surface tension at the alcohol-charcoal interface is lower than that at a water-charcoal interface and less dye can be held by it.

Further, we find that there are other forms of energy which manifest themselves at phase boundaries. These modify surface tension in addition to producing other new phenomena. Of these latter may be mentioned the effects on the compressibility of the liquid and on its properties as a solvent. Thus, J. J. Thomson states that potassium sulphate is 60 % more soluble in surface films than in the body of the water phase. Such actions on solvents are sometimes known as « lyotropic » and they play an important part in the reactions of colloidal systems. The most frequent and significant of conditions at phase boundaries, other than surface tension, are those connected with the presence of an electric charge. This charge is, in general, to be accounted for by electrolytic dissociation. Thus, in the two-phase system of sand and water, we find that the sand particles have a negative charge, the water a positive one. The sand, as an acid, may be regarded as sending off from its surface positively charged H ions to the water, but, owing to the insolubility of the anion ($Si\ O_3$), these cations cannot leave the neighbourhood of the surface on account of the great electrostatic attraction of the opposite ions fixed there. A permanent Helmholtz double layer is thus formed.

It is difficult to apply these considerations in some few cases, such as the negative charge on drops of petroleum in water. But this charge may be found to be due to traces of impurity, as in Hardy's experiments on the surface tension of similar inert liquids. In any case, the presence of this electric charge introduces another form of energy at the surface; and this can be decreased by deposition of oppositely charged ions, giving rise to the electrical form of adsorption. The mutual action of surface tension and electric charge brings about many complex states. Thus the direct effect of an electric charge is to decrease surface tension, owing to the mutual repulsion of similarly charged elements of the surface. It may happen, however, that an ion may have so great a

power of decreasing mechanical surface tension that it may be adsorbed on an electrically charged surface to such a degree as to reverse the sign of the charge thereon.

Without going into more details, it will be manifest that the state of affairs at phase boundaries may be of extraordinary complexity and probably capable of explaining a large number of phenomena as yet obscure. It may be profitable to consider a few cases in a little more detail, including those referred to at the beginning of this article.

Before passing on to these, there is one fact that we shall find later to be of some physiological significance. Surface tension is found to *decrease* as the temperature rises, or, as it is sometimes put, it has a negative temperature coefficient. If we remember that the interface between a liquid and its vapour disappears when the temperature has risen to the critical point and, with it, naturally all the phenomena associated with a boundary surface, the fact that there is a diminution of these phenomena as the critical temperature is approached is to be expected. It follows from the decrease of surface tension with rise of temperature that all those phenomena which are controlled by surface tension, such as adsorption and, in all probability, muscular contraction, suffer diminution by heat.

Suppose that we have a two-phase system of solid and liquid and that the liquid phase contains a substance in solution which is capable of entering into chemical reaction with the material of which the solid phase is composed. By adsorption, the concentration of this substance will be raised on the surface of the solid phase and, by mass action, the rate of the reaction will be increased. Further, suppose that the liquid phase contains two substances which react slowly with each other, but not with the solid phase. They will be brought into intimate contact on the surface of the latter, their concentration raised and again the rate of their mutual reaction increased. One of the reacting bodies may obviously be the solvent itself. But, in all these cases, the rate of the reaction is not given by a simple application of the law of mass action, since the active masses are not functions of the molecular concentrations, but of the surfases of the phase boundaries. The application of these considerations to the problem of the action of enzymes and of heterogeneous catalysts in general will be apparent.

That the action of enzymes is exerted by their surfaces is shown, apart from the fact that they are all in the colloidal state, by the results of experiments made in liquids in which they are insoluble, so that they can be filtered off by ordinary filter paper and the filtrate found to be free from enzyme. Notwithstanding their insolubility, enzymes are still active in such liquids. The statement has been shown to apply to lipase, emulsin, urease, invertase and peroxidase, probably to pepsin and trypsin and the only difficulty in extending it to all enzymes is that of finding a substrate soluble in some liquid in which the enzyme itself is insoluble. That adsorption is a controlling factor in the velocity of enzyme action has been advocated by myself for some years, but it is not to be understood as implying that the whole action of enzymes is an « adsorption » phenomenon; it is indeed difficult to attach any definite meaning to this statement. The rate at which the chemical reaction proceeds is controlled by the mass of the reagents concentrated on the surface of the enzyme phase at any given moment, but the temperature coefficient must be that of a chemical reaction, not that of adsorption, since the chemical reaction is the slowest member of the series of factors.

May not, then, the adsorption of the reacting substances on the surface of the enzyme suffice in itself to bring about the state of equilibrium at the increased rate characteristic of catalytic action? If so, the assumption of a secondary chemical combination between enzyme and substrate may be superfluous. More hesitation in suggesting this view for serious consideration would be necessary if it had not been given by Faraday as the explanation of one of the most familiar cases of heterogeneous catalysis, namely, the union of oxygen and hydrogen by means of the surfaces of platinum and other solids. The insight shown by Faraday into the nature of the phenomena with which he was concerned is well known and has often been remarked; so that the fact that he favoured this hypothesis is in itself evidence for its correctness. The case referred to is clearly one of those called catalytic by Berzelius. The fact that the agent responsible for the effect did not suffer permanent change in the process was apparent to Faraday. I would also, in parenthesis, call attention to the circumstance that the nature of the gold solutions which he prepared was correctly recognized as that

of a suspension of metallic particles; in other words, what we now call a colloidal solution. Although the systematic investigation of colloids, and the name itself, were due to Graham, the whole of the credit of the discovery should not be given to the inventor of the name, however great were the advances in knowledge due to him. Adsorption, also, was accurately described by Faraday, although again he did not use the name.

It must be admitted that there are, at present, difficulties in the way of accepting concentration by adsorption as a complete account of catalysis by enzymes. It is not obvious, for example, why the same enzyme should not be able to hydrolyze both maltose and lactose. Another difficulty is that it is necessary to assume that the relative concentration of the components of the chemical system must be the same on the surface of the enzyme and in the body of the solution; in other words, the adsorption of each must be the same function of its concentration. Unless this were so, the equilibrium position on the surface of the enzyme phase and consequently in the body of the solution would be a different one in the presence of an enzyme from that arrived at spontaneously or in the presence of homogeneous catalysts, such as hydrogen ions. This consideration, to which my attention was called by Professor Hopkins, requires experimental investigation. We know, indeed, that in some cases, there is such a difference in the equilibrium position, for which various explanations have been suggested. But it would be a matter of some interest to know how far this difference of equilibrium position is related to different degrees of adsorption of the components of the system.

As has been pointed out, adsorption is under the control of so many factors, surface tension, electrical charge and so on, that the possibilities seem almost innumerable. There are, moreover, two things to be remembered in this connection. Hardy has pointed out that it is probable that the increased rate of reaction at interfaces between phases may be due, not merely to increased concentration as such, but that, in the act of condensation itself molecular forces may be brought into play which result in a rise of chemical potential of the reacting substances. In the second place, Barger has shown that the adsorption of iodine by certain organic compounds is

clearly related to the chemical composition of the surfaces of these compounds, although this fact does not result in abolition of the essentially adsorption nature of the process nor in chemical combination. It would appear that those properties of the surface, such as electric charge, surface tension, and so on, which control adsorption, are dependent on the chemical nature of the surface. This dependence would naturally be expected, since the physical properties of a substance are related so closely to its chemical nature.

The facts known with regard to enzymes lead, as it seems to me, unavoidably to one conclusion. This is, that any simple application of the law of mass action cannot lead to a correct mathematical expression for the rate of reaction, although attempts of the kind have been made, as by van Slyke. The rate must be proportional to the amount of substrate adsorbed and this again is a function of the concentration both of the substrate and of the products. It is, therefore, a continously varying quantity. The differential equation must be of the type:

$$\frac{d\,C}{d\,t} = K\,C^n$$

where n itself is an unknown function of C, the concentration of the substrate or products. The hypothesis of control by adsorption gives a simple explanation of the exponential ratio between the concentration of the enzyme and its activity, expressed, however, by a different numerical value of the exponent according to the stage of the reaction. At the beginning, it may sometimes be nearly one, in the middle it approximates to one-half, as in the so-called « square-root law » of Schütz and Borissov, a law which is nearly correct for a particular stage of the change. Simple explanations are also given of the fact that increasing the concentration of the substrate above a certain value no longer causes an increased rate of reaction. This is doubtless because the active surface is saturated. Again, the effect of antiseptics and other substances, which by their great surface activity obtain possession of the surface of the enzyme phase and thereby exclude, to a greater or less degree, the adsorption of the substrate, receives a reasonable account. In many cases, the depressant or favouring effect of electrolytes, including acid and alkali,

is probably due to aggregation or dispersion of the colloidal particles of the enzyme, with decrease or increase of the total active surface.

The part played by the relative concentration of water in determining the direction of hydrolysis or synthesis in reversible reactions suggests that there are effective mechanisms in the cell by which water can be removed or added to the reacting systems. These mechanisms are probably colloidal in nature. It is known that the distribution of water between the two phases of an emulsoid colloid is very sensitive to changes in the chemical composition of the liquid phase. It appears also that adsorption of water plays a part in the phenomena known as imbibition.

Let us next devote a little attention to a more coarsely heterogeneous system, namely, that of the cell as a whole in relation to the surrounding medium. What light can we throw on the vexed question of the nature of the cell-membrane? It is quite clear that we have here a contact surface between two phases. From the nature of adsorption, there can be no doubt that, if the cell or the surrounding medium contains substances which decrease surface energy of any form, these constituents will be concentrated at the interface. Now there are many substances present in cells, of lipoid, protein or simpler nature, which have this property. Further, the experiments of Ramsden have shown that a large number of such substances are deposited in the surface film in so concentrated a degree that they become more or less rigid or solidified. We are naturally led to enquire whether this fact may not account for the existence of the cell-membrane, about which so much discussion has taken place. We find experimentally that there are facts which show that this membrane, under ordinary resting conditions, is impermeable to most crystalloids, includiug inorganic salts, acids and bases, while being permeable to water. It is, thus, an almost perfect semi-permeable membrane. There is no other possible explanation of the circumstance that the salts present in cells are not only in different concentration inside from that outside, but that there may even be complete absence of certain salts from one phase which are present in the other. Such a case is that of sodium in respect to the red blood corpuscles of the rabbit. Moreover, the experiments of Hoeber have shown that elec-

trolytes are free in the cells, so that they are not prevented from diffusion by being fixed in any sort of combination. The mere assumption of a membrane impermeable only to colloids will not account for the facts, since, as I have shown, this would only explain differences of concentration, not of composition. The view that the membrane is formed by surface concentration of cell constituents readily accounts for the changes of permeability which occur in functional activity, since its composition depends on that of the cell protoplasm and chemical changes of many kinds are taking place in this complex system.

If this membrane is actually formed by adsorption, it will be evident that we are not justified in speaking of it as a lipoid nor as a protein alone. It must have a very complex composition, varying with the physiological state of the cell itself. Indeed, complex artificial membranes have been prepared, which have properties very similar to those of the cell membrane. In short, the cell membrane is not to be regarded as an independent entity, but as a working partner, as it were, in the business of the life of the cell. In the state of excitation, there is satisfactory evidence that it loses its state of semi-permeability. This applies to muscle, nerve, gland cell and to the excitable tissues of plants. We shall presently see that the fact gives us a reasonable explanation of the electrical change associated with the state of excitation.

Another consequence which follows from the consideration of the cell-membrane as a part of the cell system as a whole is that we are not surprized to find that substances may affect profoundly, although reversibly, the activities of the cell even when they do not penetrate beyond the outer surface. The state of dynamic equilibrium between the cell membrane and the rest of the system is naturally affected by such means, since changes in one component involve compensating ones in the others. Interesting examples of such actions exerted by substances which do not get into the interior of the cell are not infrequent. I may mention the effect of calcium ions on the heart muscle, that of sodium hydroxide on oxidation in the eggs of the sea-urchin (Warburg) and that of mineral acid on the contraction of the jelly fish (Bethe).

Those drugs, such as pilocarpine and muscarine, which act only during their passage through the membrane and lose

their effect when their concentrations are equal within and without the cell are difficult to explain on any hypothesis yet suggested.

The work of Dale on anaphylaxis leads him to the conclusion that the phenomena shown by sensitized plain muscle can most reasonably be explained by colloidal interaction on the surface of the fibres. The result of this is increased permeability and excitation resulting therefrom.

The electrical change in excitable tissues and its relation to the cell-membrane has been incidentally referred to above. It was, I believe, first pointed out by Ostwald and confirmed by the work of various subsequent investigators, including myself, that in order that a membrane may be impermeable to a salt, it is not a necessary condition that it shall be impermeable to both ions. If impermeable to one of these only, the other, although diffusible, cannot pass out beyond the point at which the osmotic pressure due to its kinetic energy is balanced by the electrostatic attraction of the oppositely charged fellow ion. There is thus a Helmholtz double layer formed at the membrane, the outside having a charge of the sign of the diffusible ions, the inside that of the ions to which the membrane is impermeable.

Suppose that we take two points on the surface of a cell having a membrane with the above properties and that we connect these points to some instrument capable of detecting differences of electrical potential. It is plain that the existence of the electric charge will not be manifest, because the two points are in the same electrical state and we cannot obtain access to the internal member of the double layer without destroying the cell. But, if excitation means increase of permeability, the double layer will disappear at an excited spot, owing to indiscriminate mixture of both kinds of ions and we are then practically leading off the interior of the cell, or the internal component of the double layer, and the contacts are no longer equipotential. Since we find experimentally that a spot at rest is electro-positive to an excited one, the outer component of the double layer must he positive, that is, the membrane is permeable to certain cations, impermeable to certain anions, while in the unexcited state. Any action on the cell such as would make the membrane permeable, injury, certain chemical agents and so on, has the

same effect as the state of excitation. If we may assume the possibility of degrees of permeability, the state of inhibition might be produced by *decrease* of permeability of the membrane of a cell, which was previously in a state of excitation due to some cause, either inherent in itself or coming from the outside. This account of the electromotive changes in cells is essentially the same as that given by Bernstein.

The application of some of these facts to the problem of secretion is worth brief reference. If we suppose that the setting into play of secretory cells is associated with the production of some osmotically active substance, together with abolition of the semi-permeability of the membrane covering the ends of these cells which are in relation to the lumen of the gland alveolus, it is plain that water will be taken up from the lymph spaces and capillaries and escape to the duct, carrying with it the secretory products of the cell. The process would be continuous as long as the osmotically active substances are formed. Phenomena of this kind have been described by Lepeshkin in the case of some plants and evidence has also been found of increased permeability of the gland cells during secretion in animal organs. From what has been said above, it is unnecessary to remark that electrical differences will show themselves between the two ends of such cells, as has been found to be the case.

The modifiability of such a membrane as that formed by concentration of cell constituents is of much importance in the properties of the synapse between the neurones of the central nervous system. It allows of the manifold possibilities of permitting or blocking passage of excitation or inhibition or of being affected by chemical agents.

The numerous ways in which phenomena at phase boundaries intervene in physiological events has, I think, been made sufficiently evident. There are very few of these, if any, in which some component or other is not influenced by the effect of surfaces of contact. In conclusion, however, I may refer in a little more detail to the case of muscular contraction, with which this article commenced.

It has become clear, especially through the work of Fletcher, Hopkins and A. V. Hill, that what is usually called muscular contraction consists of two separate sets of facts. Starting from the resting muscle, we find that it has a store

of potential energy, which can be given up to do external work when the muscle is stimulated. This store must obviously be replenished again and this is effected by an independent reaction of an oxidative nature in which energy is afforded to restore the muscle system to its original state. Confining our attention, to begin with, to the actual contractile stage, the essential fact is the production of a certain amount of energy of tension, which can be utilized for the performance of external work or allowed to become degraded to heat. Blix first propounded the view that the amount of this energy is related to certain surfaces in the muscle fibres, but it was A. V. Hill who demonstrated the fact in a systematic and quantitative manner. It was shown by him that the amount of energy set free in the contractile process is directly related to the *length* of the muscle fibres during the development of the state of tension. In other words, the process is a surface phenomenon, not one of volume, and is directly proportional to the area of some surfaces arranged longitudinally in the muscle fibre. The same relationship has been shown by Patterson and Starling to hold for the ventricular contraction of the mammalian heart and by Kozawa for that of the cold blooded vertebrate. It appears that all the phenomena connected with the output of blood by the heart can be satisfactorily explained by the length of the ventricular fibres during the period of development of the contractile stress. That is, the degree of filling at the moment of contraction is the determining factor in the energy of the following systole.

Fitzgerald in 1878 suggested that surface tension itself may be responsible for the energy given off in muscular contraction and it seems, from calculations made, that changes at the contact surface of the fibrillae with the sarcoplasm may be capable of affording a sufficient amount. But the difficulties in deciding the question are great. Apart from the facts already mentioned, there is other interesting evidence at hand. It has been shown by Gad and Heymans, Bernstein and others that the contractile stress produced by a stimulus has a negative temperature coefficient. Within the limits of temperature between which the muscle can be considered to be normal, this stress is greater at a lower temperature. The same statement was shown by Weizsäcker to hold for the heat developed in this initial stage. Now, of all the forms of energy

possibly concerned, that associated with phase boundaries is the only one with a negative temperature coefficient. This relationship to temperature is also shown by the well known increase of the tonus of smooth muscle with fall in temperature.

There can be little doubt that lactic acid plays an important part in the chance of surface tension during contractile stress. This view was, indeed, put into a definite statement by Haber and Klemensiewicz in 1909, in a frequently quoted paper on the forces present at phase boundaries. The production of acid is said to alter the electrical forces at this situation. The electrical change involves one of surface tension and it is this change of surface tension that brings about the mechanical deformation of the muscle. Mines also has brought forward good reason for regarding the production of lactic acid as responsible for the change of tension in muscle. As to how the lactic acid is set free and of what nature the system of high potential energy present in resting muscle is, we are still very much in the dark. The absence of evolution of carbon dioxide in the absence of oxygen shows that no oxidation takes place in the process of the development of tension. There are, moreover, difficulties in supposing that this system present in resting muscle is of a chemical nature. If the energy afforded by the oxidation of carbohydrate in the recovery stage is utilized for the formation of another chemical system with high energy content, the theory of coupled reactions indicates that there must be some component common to both systems. It is difficult to see what component could satisfy the conditions required. On the whole, some kind of system of a more physical nature seems more probable. If it be correct that the oxidation of substances other than carbohydrate, such as fat, can afford the chemical energy for muscular contraction, as appears from certain metabolism experiments, a further difficulty arises with regard to a coupled reaction. But the question still awaits investigation.

We may conclude from the short review here presented that further study of the phenomena at phase boundaries will throw light on many problems as yet obscure. It would probably not be going too far to say that the peculiarities of those phenomena which we call « vital » are due to the fact that they are manifestations of interchange of energy between the

phases of heterogeneous systems. It was Clerk Maxwell who compared the transactions of the material universe to mercantile operations in which so much credit is transferred from one place to another, energy being the representative of credit. There are many indications that it is just in this process of change of energy from one form to another that special degrees of activity are to be observed; such, for example, are the electrical phenomena shown in the oxidation of phosphorus or benzaldehyde and it appears that the high efficiency of the photo-chemical system of the green plant is due to catching of the light energy on its way, as it were, to its degradation to heat and utilized for chemical work before this has happened. In a somewhat similar way, it might be said that money in the process of transfer is more readily diverted, although perhaps more frequently to improper use in this case. But, just as in commerce money that is unemployed is of no value, so it is in physiology. Life is incessant change or transfer of energy and a system in statical equilibrium is dead.

London.

MILANO — TIPO-LIT. REBESCHINI DI TURATI E C.

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